

THE VERTICAL FLUX OF RARE EARTH ELEMENTS IN THE  
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## ABSTRACT

Rare earth element (REE) composition of sinking particles was examined in time-series sediment trap samples collected from four depths (200, 500, 1000, 2000 m) in the Gulf of Lions. Vertical flux profiles showed the occurrence of a sedimentation pulse which resulted in the rapid sinking of phytoplankton aggregates to 2000 m depth. These particles were characterized by REE patterns similar to those in the upper 200 m indicating that little, if any, additional REE scavenging occurred during the sedimentation event. In contrast, after the sedimentation pulse, particles from deep waters showed an enrichment of light-REE (LREE) relative to heavy-REE (HREE) and a positive Ce anomaly. Comparing REE patterns in particles from the upper water column (200 m) with those from depth (1000, 2000 m) during and following the sedimentation pulse indicates that time is a key factor in determining REE scavenging by sinking particles. This is particularly evident for the preferential scavenging of Ce (IV) which is most pronounced in the finer, slowly sinking, and presumably older particles. These findings are consistent with REE patterns in sea water from the northwestern Mediterranean which show a strong negative Ce anomaly and gradual enrichment of REE with increasing atomic number. The enrichment of LREE relative to HREE in particles from deep waters results either preferential scavenging of LREE on particles, analogous to the enrichment of Ce, or selective dissolution of HREE in association with particle remineralization processes, or both; this aspect of REE behaviour merits further study.

## INTRODUCTION

Evidence from several sources indicates that surface waters of the northwestern Mediterranean are enriched in many trace elements compared to open waters outside the Strait of Gibraltar (Spivak *et al.*, 1983; Boyle *et al.*, 1985; Sherrell & Boyle, 1988; Béthoux *et al.*, 1990). A recent paper reporting data for ten rare earth elements (REE) from vertical profiles in the Mediterranean and the adjacent Atlantic demonstrates a similar enrichment of REE concentrations in surface waters within the Mediterranean basin (Greaves *et al.*, 1991). Some of the above findings,

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particularly those pertaining to biologically-essential trace elements (Boyle *et al.*, 1985; Sherrell & Boyle, 1988; Béthoux *et al.*, 1990), have been used to test vertical flux models for the biological scavenging and cycling of these elements. However, direct measurements of the vertical flux of particulate-associated trace elements which could be used to test these hypotheses have yet to be systematically undertaken in this region.

Examination of the patterns and fractionation of REE in marine waters and sinking particulate matter has provided insights into the biogeochemical behaviour of REE and particle scavenging processes in general (Elderfield & Greaves, 1982; Murphy & Dymond, 1984; Risler *et al.*, 1985; Elderfield, 1988; Masuzawa & Koyama, 1989). In the Mediterranean such studies have been confined to a limited number of water column measurements (Greaves *et al.*, 1991), neodymium isotopes (Spivak & Wasserburg, 1988; Grousset *et al.*, 1990) and REE association with suspended particulates (Risler *et al.*, 1985). One of the primary goals of Phase II of the EROS 2000 project has been to examine in detail trace element distributions in the northwestern Mediterranean in order to better understand the origin of such trace element enrichments and their subsequent cycling and transfer through the water column. From mid-April through June 1990, a sediment trap experiment was carried out in open waters of the Gulf of Lions to help elucidate these questions. We report here the first measurements of vertical particulate flux of the 14 REE at four depths (200, 500, 1000 and 2000 m) in the northwestern Mediterranean. Rare earth element patterns, concentrations and element ratios were also used to help interpret temporal and depth changes in a spring sedimentation event which took place during the experiment.

## MATERIAL AND METHODS

### Vertical Flux Experiment

From 14 April to 1 July 1990, automated time-series sediment traps (cylindro-conical type, PPS 3 TECHNICAP, 0.125 m<sup>2</sup> opening) were moored at 200, 500, 1000 and 2000 m in a 2475 m deep water column (42°N 06°E) approximately 60 nautical miles off the coast of Toulon, France. The six collection cups of each trap were timed to sample for 13 days. Preservation methodology, sample treatment and preparation of aliquots for analyses are detailed in Peinert *et al.* (this volume).

### REE Analysis

The REE were analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (VG Elemental, Winsford, Cheshire, UK). Aliquots (3-50 mg) of freeze-dried, homogenized material were placed in Teflon pressure vessels (Savillex Co.), solubilized by microwave digestion using HNO<sub>3</sub>:HF (1:2), the lids of the digestion vessels removed and the contents evaporated to dryness. Each sample was treated with a second aliquot of HNO<sub>3</sub> and evaporated to dryness before final dilution (10 ml). Samples, standards and blanks contained 2% (v/v) HNO<sub>3</sub> and 50 ppb In added as an internal standard. All acids used were Suprapur grade (Merck, France) and preparations performed under a positive pressure, laminar flow cabinet. Standard solutions were prepared by successive dilution of a stock multi-element standard (XVG-2; Spex Industries, Inc.) and analyzed along with groups of samples and blanks. Single element standards (PLK-30 element kit; Spex Industries, Inc.) were used to monitor intensities of polyatomic interferences and calculate correction factors for spectral overlap.

The precision of replicate analyses was  $\pm 5\%$  for all REE's with the exception of Eu (10-20%) and Gd (variable). The loss of precision for Eu in these samples was caused by overlap of BaO on the analyte signal. Large correction factors (3-30%) were used to compensate for the BaO signal intensity.

## RESULTS AND DISCUSSION

Vertical mass fluxes at the four depths during the 10-week period are shown in Figure 1. The fluxes varied greatly over time but all fall within the range of values which have been reported for other offshore stations in this region of the northwestern Mediterranean (Fowler *et al.*, 1987; Buat-Menard *et al.*, 1989). The most striking feature was a major pulse of

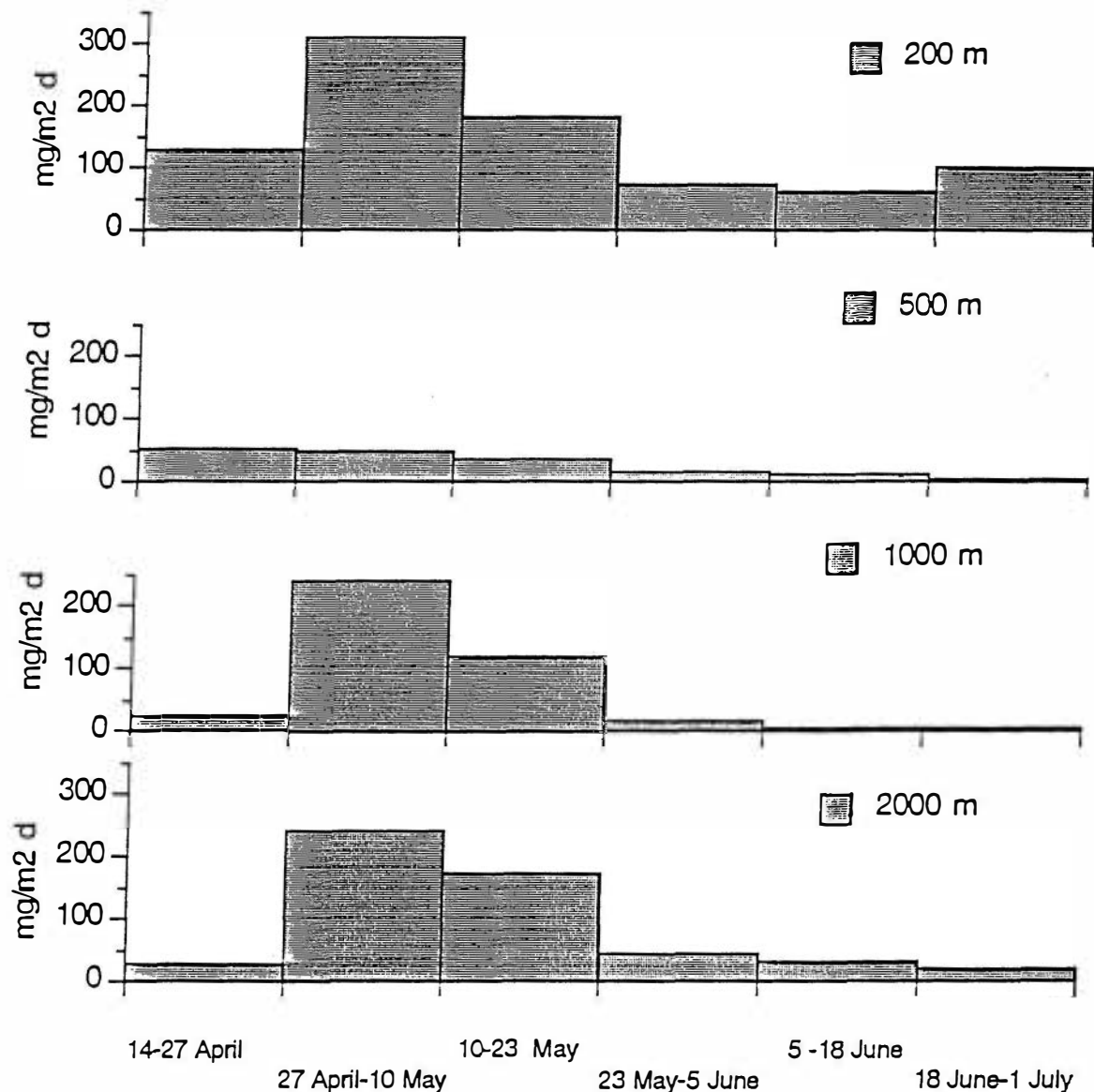


Fig. 1. Temporal variation in mass flux ( $\text{mg dry m}^{-2}\text{d}^{-1}$ ) through four depths at the EROS-2000 station in the Gulf of Lions ( $42^{\circ}\text{N}$ ,  $06^{\circ}\text{E}$ ) during April-June 1990.

particle flux which occurred between 27 April and 10 May. With the exception of the 500 m trap (see Peinert *et al.*, this volume), this pulse was recorded at all depths indicating very rapid transport ( $>140 \text{ m d}^{-1}$ ) of primary particles from 200 to 2000 m. Peinert *et al.* (this volume) present evidence to show that the particulate pulse was due to the collapse of a spring bloom with subsequent rapid sinking of phytoplankton-derived aggregates. Such an event of mass sinking has not been previously documented for the presumed oligotrophic waters of the Mediterranean Sea.

Rare earth elements were not measured in sea water at the mooring site. However, it is instructive to examine REE concentrations and shale-normalized patterns in filtered sea water sampled at a nearby station ( $40^{\circ}15'N$   $05^{\circ}22'E$ ) during April 1983 (Greaves *et al.*, 1991). First, the surface sea water concentrations of all ten REE analyzed were approximately two-fold higher than those measured in the adjacent Atlantic sea water. Second, as shown in Figure 2, sea water from a depth range covering that of our traps is enriched in heavy REE compared to the light-REE. Third, there is a strong negative Ce anomaly evident at all depths which is indicative of scavenging of Ce by particles and subsequent removal from northwestern Mediterranean waters.

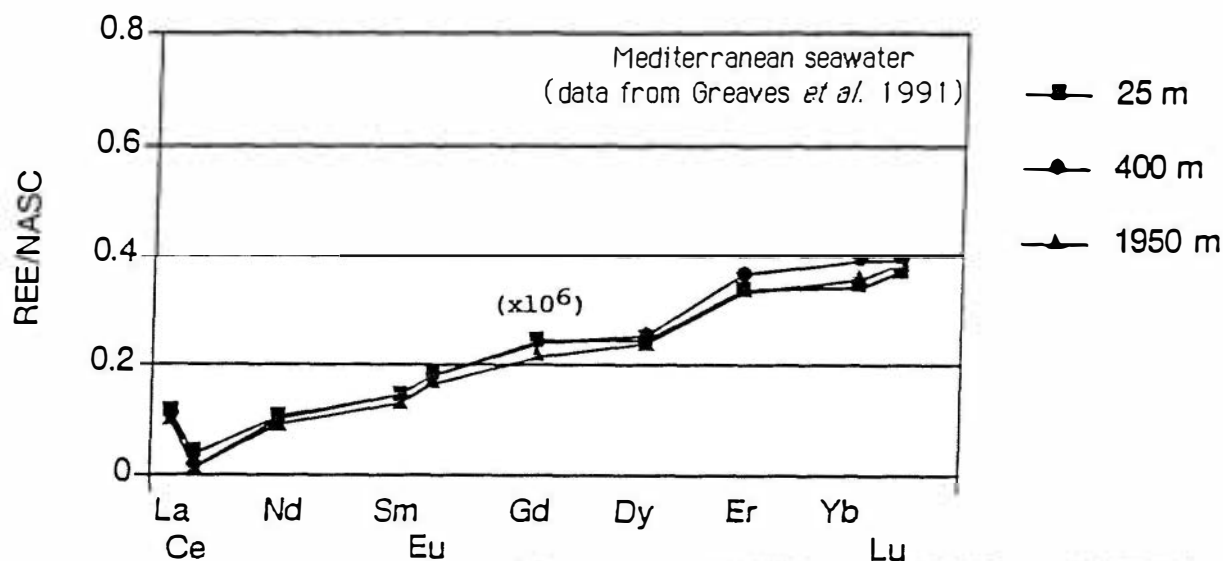


Fig. 2. Shale-normalized REE abundance patterns in sea water from three depths at a location in the northwestern Mediterranean ( $40^{\circ}15'N$ ,  $05^{\circ}22'E$ ) during April 1983. Computed values are based on REE concentration data from Greaves *et al.* (1991).

The REE concentrations in sinking particles are given in Table 1. REE fluxes can be computed by multiplying the mass flux by the corresponding REE concentrations in Table 1. In certain series towards the end of the study when particulate flux was very low, there was insufficient sample available for REE analysis. Nevertheless, from all data collected at the different depths, a regular increase in REE concentrations with depth is evident, particularly in the case of the light-REE. This trend in light-REE enrichment with depth is seen more clearly by examining light-REE/heavy-REE concentration ratios as well as computed Ce excess values (Table 2).

**TABLE 1.** Temporal variation in mass flux and corresponding REE concentrations in particles collected by sediment traps at four depths in the Gulf of Lions during spring-early summer 1990.

Depth (m)	Mass Flux (mg m <sup>-2</sup> d <sup>-1</sup> )	Concentration (nmol g <sup>-1</sup> )													
		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
<b>Series I (14-27.04.90)</b>															
200	128	27.9	49.1	6.11	22.2	4.13	0.79	3.00	0.45	3.01	0.52	1.49	0.18	1.30	0.15
500	55	25.3	52.8	5.94	20.9	4.00	0.88	3.38	0.49	2.78	0.55	1.44	0.19	1.36	0.18
1000	24	62.4	142	14.9	51.2	9.29	2.09	8.07	0.99	6.09	1.12	3.05	0.43	2.91	0.38
2000	28	71.4	165	16.6	57.0	10.1	2.33	7.80	1.06	6.09	1.17	3.24	0.45	3.05	0.39
<b>Series II (27.04-10.05.90)</b>															
200	309	25.2	41.7	5.93	22.1	4.36	0.90	3.39	0.55	3.45	0.64	1.72	0.22	1.51	0.20
500	49	33.6	63.0	7.83	28.9	5.58	1.17	4.29	0.68	4.29	0.77	2.09	0.26	1.82	0.23
1000	242	42.9	80.8	10.1	37.2	7.11	1.50	5.34	0.86	5.08	0.95	2.62	0.35	2.25	0.30
2000	241	46.6	88.6	10.7	38.8	7.08	1.47	5.43	0.84	5.24	0.95	2.67	0.34	2.21	0.31
<b>Series III (10-23.05.90)</b>															
200	182	15.8	26.8	3.61	14.4	2.63	0.54	2.30	0.31	2.26	0.40	1.16	0.13	1.08	0.12
500	36	24.3	48.9	5.70	20.4	4.00	0.92	3.85	0.49	2.98	0.55	1.50	0.21	1.40	0.19
1000	121	48.1	99.8	10.8	39.2	7.28	1.45	5.43	0.87	5.06	0.98	2.67	0.35	2.29	0.31
2000	174	55.0	113	12.4	45.6	8.38	1.61	6.06	0.91	5.66	1.09	2.98	0.41	2.70	0.37
<b>Series IV (23.05-05.06.90)</b>															
200	72	21.6	41.0	5.05	18.7	3.62	0.67	2.81	0.44	2.64	0.51	1.46	0.19	1.26	0.18
500	17	38.7	83.2	9.03	33.3	6.29	1.51	6.16	0.73	4.56	0.83	2.50	0.28	2.16	0.22
1000	16	73.4	172	17.0	61.2	11.1	2.29	12.1	1.24	7.37	1.37	3.76	0.52	3.46	0.47
2000	46	95.0	216	21.9	77.9	14.0	2.89	13.2	1.50	8.90	1.66	4.54	0.66	4.16	0.57
<b>Series V (05-18.06.90)</b>															
200	61	22.3	41.3	5.08	19.4	3.72	0.74	2.93	0.47	2.92	0.57	1.68	0.21	1.54	0.22
500	13	46.5	99.3	10.8	39.8	7.53	1.67	9.20	0.88	5.52	0.97	2.75	0.38	2.53	0.34
2000	33	130	299	29.6	105	18.5	3.76	16.9	1.93	11.1	2.12	5.78	0.82	5.22	0.71
<b>Series VI (18.06-01.07.90)</b>															
200	101	20.8	35.7	5.00	19.0	3.69	0.79	2.97	0.48	3.02	0.57	1.62	0.22	1.45	0.21
2000	19	144	331	33.0	117	20.7	4.13	18.4	2.13	12.4	2.39	6.49	0.94	5.86	0.82

**TABLE 2.** Light-REE and heavy-REE concentration ratios and the computed excess Ce content in particulate samples from sediment traps at four depths in the Gulf of Lions during spring-early summer, 1990.

Depth (m)	LREE/HREE	Ce <sub>(ex)</sub>
<b>Series I (14-27.04.90)</b>		
200	1.54	-14.0
500	1.41	-4.3
1000	1.62	1.2
2000	1.73	3.2
<b>Series II (27.04-10.05.90)</b>		
200	1.25	-15.2
500	1.37	-13.0
1000	1.40	-16.3
2000	1.48	-16.7
<b>Series III (10-23.05.90)</b>		
200	1.17	-9.0
500	1.31	-6.1
1000	1.49	-8.9
2000	1.49	-11.0
<b>Series IV (23.05-05.06.90)</b>		
200	1.26	-7.9
500	1.34	-4.3
1000	1.57	6.6
2000	1.67	1.1
<b>Series V (05-18.06.90)</b>		
200	1.09	-9.0
500	1.39	-5.9
2000	1.79	5.0
<b>Series VI (18.06-01.07.90)</b>		
200	1.10	-11.3
2000	1.77	4.9

For the purpose of computation, LREE include the sum of normalized concentrations of La, Pr, Nd and Sm, and the HREE include Er, Tm, Tb and Lu. The excess cerium content (Ce<sub>(ex)</sub>) is computed from the equation  $Ce_{(ex)} = Ce - La (Ce/La)_{NASC}$ .

Most instructive of the temporal changes taking place during the experiment is a detailed examination of the REE abundances in settling particles normalized to North American Shale Composite (NASC). Several features are evident in the time-series data set shown in Figure 3. First,

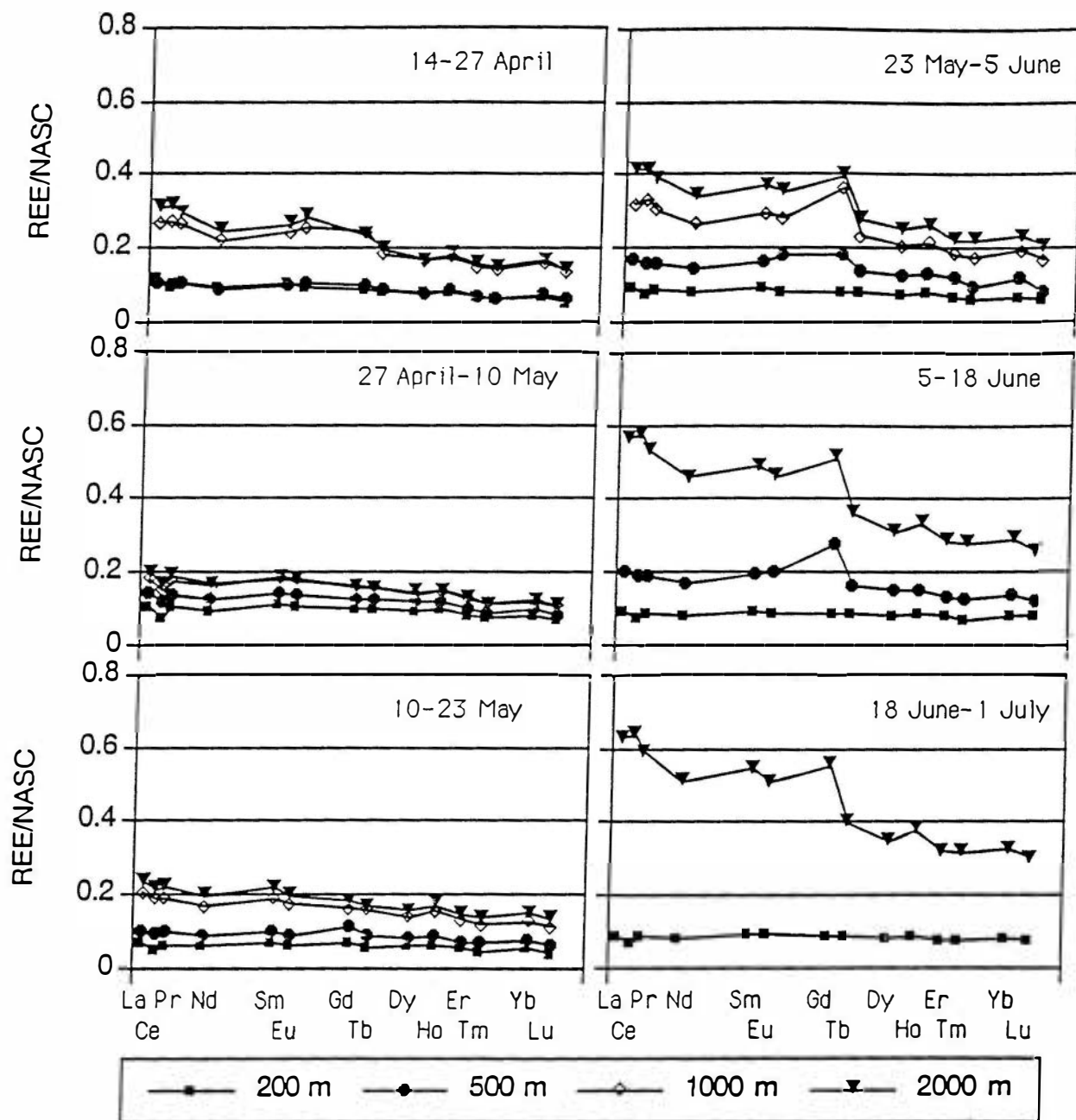


Fig. 3. Shale-normalized REE abundance patterns in time-series sediment trap samples from the EROS-2000 sediment trap station in the Gulf of Lions. Each series represents a 13-day collection interval.

REE patterns in the sinking particles do not at all reflect the pattern characteristic for Mediterranean sea water (Fig. 2). The patterns in particles are either flat, particularly in the upper water column, or show an enrichment of light-REE relative to the heavy-REE in the samples from deeper waters. This is consistent with REE patterns reported for fluxing

particles in the Japan Sea (Masuzawa & Koyama, 1989) but contrasts markedly with observations from the eastern equatorial Pacific where heavy-REE enrichments were noted in sediment trap material similar to those characteristic of sea water (Murphy & Dymond, 1984). Second, REE concentrations in particles increase with depth similar to the trends which have been observed in the two other sediment trap studies in the Pacific Ocean (Murphy & Dymond, 1984; Masuzawa & Koyama, 1989). This general increase in concentration is less pronounced during the second and third series of measurements when particle flux was at a maximum due to the crash of a phytoplankton bloom. In this case the patterns were flat and displayed less variation in REE concentrations with depth indicating the similar chemical nature of material collected at all depths. During this time, the samples at all depths showed a negative Ce anomaly much like that observed in sea water. The Ce signal is apparently acquired by particles in the upper water column (e.g., 200 and 500 m, Fig. 3) and remains essentially unchanged when descent is very rapid and there is insufficient time for further scavenging of Ce by the particles. However, after the major flux event ceased in late May, the particulate samples from deep waters, where mass flux was low, all displayed light-REE enrichment relative to heavy-REE and a clear positive Ce anomaly. During this time, the particles from the upper water column were sinking very slowly and had sufficient time to scavenge additional Ce which resulted in a positive Ce anomaly. This trend in Ce enrichment on particles, which has also been reported for sediment trap samples from the Japan Sea (Masuzawa & Koyama, 1989), is consistent with the notion that the scavenging of oxidized Ce (IV) by sinking particles is both time-dependent and microbially-mediated (Moffett, 1990). Hence, the slowly sinking and presumably finer particles we measured showing characteristic-enhanced REE concentrations and strong positive Ce anomalies, closely mirror REE patterns in the suspended particulate fraction filtered from northwestern Mediterranean waters (Risler *et al.*, 1985). From this initial assessment, we conclude that the different Ce anomalies noted in sediment trap collections may be a reflection of particle size and, hence, overall residence time in the water column.

In the case of the light-REE enrichments noted in the deeper particle samples, factors other than scavenging may be involved. For example, if REE scavenging is dominated by organic particles, it would be expected that most REE fractionation would take place in the biologically-rich, surface waters and not at depth as suggested by the gradual increase in the light-REE to heavy-REE concentration ratios we observed. In addition, remineralization of biogenic particles is known to occur in deep waters but this process does not necessarily lead to further fractionation of REE (De Baar *et al.*, 1991). The only exception is Ce because of its unique redox chemistry. Thus, particle remineralization processes could equally be time-dependent and thereby provide another mechanism for increasing the relative concentration of the trivalent REE in particles with increasing water depth. For these reasons, it is difficult to attribute a specific cause for the relative enrichment of light-REE in the deep samples; however, it is likely related to either preferential scavenging of light-REE, remineralization and selective dissolution of HREE from biogenic and non-biogenic particles, or both.

Of equal interest is the strong positive gadolinium anomaly observed in some of our deeper samples (Fig. 3). To our knowledge, this is the first time such anomalies have been reported in marine particulate material. As in the case of Ce, the gadolinium anomaly was not observed in particulate samples collected during periods of high flux (27 April - 23



May, Fig. 3). This finding, if true, likewise suggests that gadolinium scavenging relative to that of its nearest neighbours, Eu and Tb, is a time dependent process. Why this should occur is far from clear. Positive gadolinium anomalies in sea water have been reported previously (De Baar *et al.*, 1985) and were thought to result from the higher degrees of solution complexation of Gd relative to its neighbouring members. However, in a more recent assessment, De Baar *et al.* (1991) suggest that surface organic ligand complexation also plays an important role in the scavenging of Gd relative to Tb and Eu. In fact, our samples collected during late spring-early summer were primarily biogenic, displayed high POC/chlorophyll *a* ratios and were rich in zooplankton feces (Peinert *et al.*, this volume). Nevertheless, we presently have some doubts about the validity of our Gd measurements performed by ICP-MS. The sediment trap material was rich in Ba and Al, and the presence of high concentrations of Al in evaporated digests appears to retain sufficient fluoride to form a polyatomic ionized species with Ba (e.g.  $^{138}\text{Ba}^{19}\text{F}$ ) which overlaps with the analyte signal for  $^{157}\text{Gd}^+$  as used in our analytical procedure. If this is the case, then the apparent Gd anomaly shown in some REE patterns of the deep water trap samples (see Fig. 3) could be caused by an analytical artifact. We are presently examining this possibility in more detail.

The only two published studies on REE in sinking particles do not present results for Gd (Murphy & Dymond, 1984; Masuzawa & Koyama, 1989). The data of Greaves *et al.* (1991) do not indicate a Gd anomaly in sea water from near our sediment trap station. However, if our Gd data are verified, then the strong positive Gd anomaly observed in our deep samples (500-2000 m) from 23 May onward is not consistent with the contention of De Baar *et al.* (1991) that Gd has a lower affinity for particles and thus should remain preferentially in sea water solution compared to its neighbours. Clearly, Gd scavenging behaviour would benefit by further measurements of the REE suite in sea water and particulate samples collected simultaneously from the same location and depths.

Coupling our flux measurements with the water column data of Greaves *et al.* (1991), it is possible to derive reasonable estimates of REE residence times for this region of the northwestern Mediterranean. Computed residence times for the upper 200 m and 2000 m water column are given in Table 3. Values for the upper 200 m where biological activity is greatest, are relatively short ranging from 1.7 to 24 years. Residence times increase with increasing mass number, except for the case of Ce

**TABLE 3.** Computed REE residence times (years) in the upper 200 m and 2000 m in the open northwestern Mediterranean.

Depth (m)	*Residence Time (y)									
	La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb	Lu
200	4.7	1.7	5.0	6.0	7.9	11	12	19	19	24
2000	24	4.0	27	34	48	62	85	130	140	160

\* Computation is based on the water column inventories (0-200 m and 0-2000 m) of the REE (Greaves *et al.*, 1991) at a location (40°15'N, 05°22'E) not far from the EROS 2000 sediment trap station (42°N, 06°E). Average yearly REE fluxes through 200 and 2000 m are computed from the six consecutive measurements for those depths made at the EROS 2000 station (see Table 1).

whose redox chemistry results in enhanced scavenging and hence, a very short residence time in the upper mixed layers. Using the 2000 m inventory, which covers nearly the entire water column, residence time values are accordingly longer, but nevertheless, follow the same tendency to increase with increasing weight of the element. The short residence time of 4 years for Ce relative to the other REE is strong evidence for its rapid removal from the entire water column in the northwestern Mediterranean. It should be kept in mind that our estimates are based on a single data set of water column concentrations and flux measurements that spanned only 10 weeks of the year. It is certain that these values will be revised when more data over longer time scales become available.

## CONCLUSION

The temporal changes in REE composition of sinking particulate material at different depths were used to describe REE scavenging behaviour in northwestern Mediterranean waters. Time has been identified as a key variable in determining the relative enrichments of REE on particles during their descent through the water column. Fresh, primary particles formed in the upper layers, more closely reflected the REE signature found in ambient sea water, in particular a negative Ce anomaly. When these particles sank rapidly (100's m d<sup>-1</sup>) as biogenic aggregates, a similar REE pattern was found in this material at depth. This observation underscores the speed with which a collapsing phytoplankton bloom sank to 2000 m in this part of the Mediterranean during spring 1990. During subsequent periods when vertical flux was low and sinking speeds were concomitantly slower, enhanced scavenging by particles occurred resulting in enrichment of light-REE relative to heavy-REE as well as a positive Ce anomaly. The positive Ce anomaly associated with these particles agrees with the hypothesis that Ce (IV) is preferentially scavenged by sinking particles in Mediterranean waters (Greaves *et al.*, 1991). On the other hand, the apparent positive Gd anomaly observed in the same particulate samples, if real, is not consistent with current hypothesis regarding the origin of positive Gd anomalies reported for sea water (De Baar *et al.*, 1991), and, hence, needs further detailed study.

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